Questions About PVC

FIVE QUESTIONS FOR ANDRÉ ROLLIN: FUNCTIONAL PVC GEOMEMBRANES

GFR: Regardless of the application for which a geomembrane is used, we often refer to the geomembrane by its general category, such as "a PVC geomembrane," and leave it at that. But this really does not say enough. In the case of PVC, what is its core composition? And how does this affect its many formulations?

AR: Polyvinyl chloride (PVC) has been produced since 1835. In 1932 a plasticizer that could be added to the PVC formulation resulted in the production of a wide range of flexible products. Flexible PVC geomembranes were introduced to the market in the 1950s.

PVC is produced from petroleum fractions (ethylene and acetylene) and chloride by means of a suspension polymerization performed in reactors where vinyl chloride and an initiator are dispersed in water. Reaction time and temperature are set to control the molecular weight of produced chains (polymerization levels). Since PVC is a rigid material, a plasticizer that can lower attraction forces between hydrogen and chloride molecules is incorporated to lower the brittleness temperature. A PVC flexible material is composed of crystalite areas surrounded by amorphous areas into which the plasticizer is located. The maximum quantity is controlled by the desired permeability of the product – generally in the range of 28 to 35% by weight.

Plasticizer is not the only product added to a PVC geomembrane blend: Heat stabilizers, color pigment, lubricant, biocide and others ingredients are added to resist solicitations. A PVC geomembrane must be considered as a complex recipe incorporating many ingredients in proportion, such as 35% polymer, 28 to 35% plasticizer, 0 to 20% filler, 5 to 10% of antioxidants, and 2 to 3% of other products. The proportion and quality of the ingredients in a blend can be set to match climatic conditions, nature of stored liquids and other parameters. Functional formulations of PVC geomembrane can be achieved to offer characteristics differing greatly from one product to another. The end product might be for general use, potable water storage, organic liquid storage (industrial effluents), fish grade, underground applications (transparent for tunnels, without ultra violet [UV] stabilizers), cold temperature, reinforced materials, and exposed applications (UV-protected).

GFR: That's quite a bit, but it underscores how complex the construction of a single membrane can be, and why it is important for engineers to look into the deeper aspects of material selection. How do these formulations change the vital characteristics of a PVC geomembrane so that we can achieve what we need to with our designs?

AR: In the past, inappropriate PVC formulations may have resulted in premature failures, discouraging the use of PVC geomembranes. With the understanding of the interaction between ingredients, a designed formulation can be specified for an application to offer more-than-satisfactory long-term service life.

Let's take the material apart and understand it by looking at its ingredients. First, the *molecular weight* (MW) of the PVC resin. The resin's molecular weight affects the maximum tensile strength, the tensile modulus at 100% elongation and the puncture resistance. For example a 10% increase in these properties were reported by Diebel (2002) when the MW of the resin was increased from a 69K resin to an 81K resin. The tear did not change significantly and the elongation dropped by approximately 10%. This shows that there is a balance between strength and flexibility.

In actual use, the lower MW polymer may move more easily if the substrate settles. The higher MW resin is a larger polymer resulting in greater entanglement, restricting movement.

Then we have *plasticizers*. This is the most important additive, the one that truly establishes the geomembrane's properties and chemical resistance. Two families of products are used: one, monomers such as the phtalales incorporated with geomembranes that will be in contact with drinkable water; and, two, polymers such as vinyl acetate for geomembranes in contact with organic liquids. Plasticizers used in PVC are either polymers or monomers. The monomers are different types of esters, while the polymers (often referred to as polymerics) are usually polyesters, nitrile rubbers or ketone ethylene ester polymers.

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The majority of plasticizers used in flexible PVC are monomeric phthalates. Linear phtalates are recognized as being the more stable plasticizers (less migration toward outside surfaces) because of strong bonds between the linear chains and the PVC molecules. These high leach-resistant plasticizers are used presently for the production of all geomembranes that will be in contact with water.

Monomeric trimelatate plasticizers are often used where high temperature resistance is required. For conditions under 50° C (122° F) monomeric phthalates with a chain length greater than 7 are adequate. Monomeric phthalates with chains less than 9 and adipates have poor high temperature resistance.

Polyester polymeric plasticizers are used when unique properties are required such as in the containment of oils. Resistance to animal fat, mineral oil and corn oil all have been found to degrade adipates plasticizers, indicating that they should be avoided in the containment of oils. Branched phthalates have performed slightly better than linear phthalates, while polyester polymeric plasticizers have performed the best for oils. Formulations that incorporated the polyester polymeric plasticizers have been found to perform adequately in contact with hexane (a solvent that is known to aggressively extract monomeric plasticizers), gasoline, kerosene, ASTM fuel C and ethanol. Alloys of PVC, which contain nitrile rubbers, or ketone ethylene ester polymers, have also been found to provide superior resistance to oils and grease and many other hydrocarbons. In environments where primary containment of numerous types of hydrocarbons are require, these PVC alloys would likely function well.

Also, polyester polymeric plasticizers have performed well in other aggressive environments. In concentrated caustic environments (20% sodium hydroxide solution), formulations containing the trimelatates or the polyester polymeric plasticizers had no change, while the adipates performed poorer than the monomeric phthalates.

Now we come to *stabilizers*. Mixed metal stabilizers are required in PVC formulations to allow the material to be processed into a film. A 2002 study found no significant difference in physical properties between a barium cadmium stabilizer and a barium zinc stabilizer. Both metal stabilizers are known to work synergistically with a co-stabilizer, epoxidized soybean oil (ESO). ESO is required for optimum stability and the amount of ESO does not significantly affect the physical properties.

Then we have *fillers*. Calcium carbonate is often used as a filler in plastics. Depending on the amount used in a blend, calcium carbonate can increase the modulus, increase the hardness and at very high loadings decrease the cost of the formulation. It was found that at levels less than 7% by weight the physical properties were not significantly affected and that, at levels over 20%, the physical properties were compromised and the chemical resistance severely compromised.

Stanford et al. (1979) showed that high filler loadings resulted in excessive weight gain and, thus, poor chemical resistance. A PVC formulation incorporating high calcium carbonate amount is by far the most significant negative factor in acidic leachate environments. When exposed to acidic leachates, and with 37% HCl, formulations with less than 7% calcium carbonate, incorporating a branched or linear phthalate, had less than 5% weight change and – more importantly – were still very flexible.

Now let's examine *UV absorbers and inhibitors*. Clear PVC has poor UV-light resistance, and is not recommended for extended outdoor applications without additional components that can prolong the outdoor UV exposure. These additives are UV inhibitors and absorbers or pigments. Once a small amount of pigment is added, the UV resistance improves dramatically. UV inhibitors and/or UV absorbers offer long term protection.

Next, *biocide*. The biological resistance of flexible PVC geomembranes has often been questioned and the phthalate plasticizers have been thought to be a food source for microorganisms. This was not found to be the case. Normally, flexible PVC incorporates a biocide as an extra precaution when blends include certain types of plasticizers that are more susceptible to attack. In many cases the biocide is not required since the individual raw materials were shown to be resistant to microorganism metabolism.

In a study by Klausmeir and Andrews (1981), all the different ingredients in a flexible geomembrane formulation were subjected to ASTM G21. This involves inoculating the individual raw materials with an assortment of naturally occurring fungi and then incubating the samples for four weeks in an environment where the fungi are known to thrive. None of the raw materials were found to be easily metabolized by the fungi. The monomeric phthalate had no evidence of attack by the fungi, but the adipates and sebacates are susceptible to biological growth; and, thus, should be avoided.

Overall, PVC geomembranes should be selected with formulations specific to a project's conditions. While a minimum molecular weight of 69K PVC resin is required, there is no advantage to go beyond that in most cases. Polyester polymeric plasticizers result in superior resistance to hydrocarbons while monomeric adipate plasticizers should be avoided in flexible PVC geomembranes since they have poor long-term aging and chemical-resistance properties. Monomeric trimelatate plasticizers have performed very well and are a good choice for buried, flexible PVC geomembranes, especially where sustained high temperatures (greater than 50° C) are anticipated. Branched, linear or a blend of monomeric phthalates with a carbon chain average that's greater than seven will perform well in most flexible PVC geomembrane applications. Branched phthalates performed better than linear phthalates in extremely acidic and caustic environments.

Calcium carbonate filler loadings of greater than 7% should be avoided in low pH (acidic) environments.

Proper pigment type and loading level or UV absorbers and inhibitors are required for exposed applications. Properly formulated flexible PVC is not prone to microbiological attack.

GFR: What are the most common misconceptions in the selection of a PVC geomembrane? Why should an engineer select (or not select) this material?

AR: The first misconception is that there exists only one type of PVC. This is very wrong. There are a multitude of formulations that result in an array of PVC geomembranes to fit most applications [as noted in response to the preceeding questions].

The second most common misconception is that PVC will not resist hydrocarbons, acids and bases; but, yes, PVC can resist many hydrocarbons (except strong solvents), acids and bases for a long period of time if the proper formulation is used.

Also, many seem to think that PVC will be punctured easily. On the contrary, PVC is less easily punctured than a rigid geomembrane because PVC has a high elongation characteristic – flexibility is the most desirable property of a PVC geomembrane, offering no re-alignment of the molecular chains when elongated. It conforms easily to sites, and in most applications does not require reinforcement.

A fourth misconception is that you should compare geomembrane thickness, even between disparate materials, when making a selection. This is wrong. Comparing geomembrane thickness can be irrelevant. Performance is what matters. For example, comparing the properties of a 60 mil rigid geomembrane to the properties of a 60 mil PVC geomembrane is like comparing nonwoven to woven geotextiles. At like thicknesses, the results can be dramatically different and confuse the real objective of a design. Consider that many agencies (such as New York's Department of Transportation) recognize that though nonwoven geotextiles generally have lower strength characteristics than woven geotextiles, the behavior of nonwovens is acceptable, even desirable in many applications because of higher flexibility (elongation). In many geomembrane designs, a lower thickness PVC geomembrane can offer functional performance similar to thicker, rigid geomembranes.

A fifth misconception with PVC geomembranes is that a chemically bonded seam is less resistant that a fusion seam. This is not the case if proper bonding procedure are followed. I and many others in the field have observed very strong, tensile-resistant, chemically bonded seams even after many years of their service life.

A sixth misconception is that the fragility temperature is too high. In most applications the PVC geomembrane will be covered, and a liner temperature lower than 30° C (86° F) will not be attained. Canadian and American users are well-aware that PVC membranes used as exterior pool liners can withstand very cold temperatures for many winters (more than 10 years) without cracking or suffering structural damages.

A seventh misconception is that a seam cannot be checked properly. Yes, seams can be checked properly, which is to say they allow both non-destructive and destructive testing options. For non-destructive measures, dual-fusion seams can be checked using the channel air pressure test similar to the one use for other types of geomembranes. And chemical seams must be checked using an air lance and/or electrical leak detection techniques. Destructive testing can be performed on both type of seams to measure the tensile and peel resistances.

Finally, there is a misconception that you cannot use PVC for exposed applications. Well, yes and no – the general usage product's blend (i.e., without UV inhibitors or absorbers) cannot resist long exposures; but, UV-resistant formulations will resist breakdown and perform very well for many years.

GFR: What recommendations would you make to avoid these errors?

AR: First, increase the mentorship in consulting firms and governmental agencies. In my experience, senior engineers accept project management responsibilities or move to other firms; thus, leaving junior engineers to select liners for an application without the senior engineer having transmitted their geosynthetic knowledge or the importance of analysis and proper geomembrane selection for construction. As a result, the geomembrane selection is too often associated to cut-and-pasting from past experience (which may be little). This ignores the need to take into account the availability of many other types of products – not just PVC geomembranes – that could offer the desired characteristics for safe and functional performance. In short, more education is needed. Engineers must share knowledge.

Also, on the technical side, research and development professionals must offer mentoring to the geosynthetic family members, and share educational efforts with them. For example, the PVC geomembrane industry and the various geosynthetic associations and societies. In regards to PVC geomembranes, these groups must invest time and effort to make available technical references and papers on the necessity to formulate and select the appropriate PVC geomembranes for different types of applications. Furthermore, they must make available specifications for these applications, support more seminars and courses, and never avoid giving engineers the technical, accurate information on the performance of the geomembrane. That is how we can avoid misconceptions.

GFR: We would be remiss if we did not note your 2002 book on the subject of geomembrane formulations and uses. However, a copy has appeared only in French. Is an English language version in the works?

AR: The book – *Geomembranes: a guide de choix* – was co-authored with Pierson and Lambert and published in French by Presse Internationale, Ecole Polytechnique. Since then it has been updated, and it is now in the process of being translated into English

with the collaboration of Barry Christopher, a fourth author. The English title, *Geomembranes: a guide to material selection*, should be available by the Geo-Frontiers 2005 congress [January in Austin, Texas – see page 13].

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